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**In re patent application of**

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**For: RELEASE FILM FOR PRINTED WIRING BOARD PRODUCTION**


Commissioner for Patents

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**STATEMENT UNDER 37 C.F.R. 1.55**

Sir,

I, Katsuya TAKENAKA, hereby declare that I am conversant with both English and Japanese languages, and certify to best of my knowledge and belief that the attached is a true and correct English translation of Japanese Patent Application No. 2003-113843 filed in the Japanese Patent and Trademark Office on April 18, 2003 in the Japanese language.



Katsuya TAKENAKA

Date: November 15, 2007

[Designation of Document] Specification

[Title of the Invention] MOLD RELEASING FILM FOR PRINTED  
CIRCUIT BOARD PRODUCTION

[Claims]

[Claim 1]

A mold releasing film for printed circuit board production, which is a monolayer film comprising a resin composition containing (A) a polyphenylene ether-based resin in an amount of 50 wt% or more.

[Claim 2]

A mold releasing film for printed circuit board production, which is a monolayer film comprising a resin composition containing (A) a polyphenylene ether-based resin in an amount of 50 to 99.5 parts by weight and (B) a liquid crystalline polyester in an amount of 0.5 to 50 parts by weight.

[Claim 3]

The mold releasing film for printed circuit board production according to claim 2, having a resin composition containing (C) a compound containing monovalent, divalent, trivalent or tetravalent metal element, in an amount of 0.1 to 10 parts by weight per 100 parts by weight of the total weight of components (A) and (B).

[Claim 4]

The mold releasing film for printed circuit board production according to claim 3, characterized in that the monovalent, divalent, trivalent or tetravalent metal element (C) is a Zn element and/or Mg element.

[Claim 5]

The mold releasing film for printed circuit board production according to any one of claims 2 to 4, having a resin composition containing (D) a silane compound in an amount of 0.1 to 5 parts by weight per 100 parts by weight of the total weight of components (A) and (B).

[Claim 6]

The mold releasing film for printed circuit board production according to claim 5, characterized in that the silane compound (D) has an amino group.

[Claim 7]

The mold releasing film for printed circuit board production according to any one of claims 1 to 6, characterized in that the monolayer film is obtained by molding through an extrusion tubular method.

[Claim 8]

The mold releasing film for printed circuit board production according to any one of claims 1 to 6, characterized in that the monolayer film is obtained by molding through a T-die extrusion method.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a mold releasing film suitable for production of flexible printed circuit boards, which has a polyphenylene ether-based resin composition, and is excellent in mold-releasing property, flame resistance, anti-moisture absorbing property, heat resistance, and rigidity.

[0002]

[Prior Art]

In the production step of printed circuit boards, flexible printed circuit boards, multilayer printed circuit boards, and the like, a mold releasing film is used at the time when a copper-clad laminate or a copper foil is hot-pressed through a prepreg or a heat-resistant film. Moreover, in the production step of flexible printed circuit boards, a method of inserting a mold releasing film is widely performed for the purpose of preventing adhesion of a cover-lay film to a pressing hot plate at the time when the cover-lay film is subjected to hot press bonding using a thermosetting adhesive to a flexible printed circuit board main body where electric circuits are formed.

Recently, in view of increasing social requests for environmental problems and safety, flame resistance, anti-moisture absorbing property and rigidity have been required for the mold releasing films in addition to the functions such as heat resistance for enduring hot pressing and mold-releasing property from printed circuit boards and hot pressing plates. The absorption of moisture may cause blisters by generation of water vapor during the hot pressing. When rigidity is low, the film tends to be wrinkled and suffers from a problem of poor workability.

[0003]

However, polymethylpentene films, silicone-coated polyester films, fluorine-based films, and the like which are hitherto used as mold releasing films do not sufficiently satisfy the above performances required for a mold releasing film. Namely, polymethylpentene films have insufficient heat resistance and flame resistance. The silicone-coated polyester films have an insufficient heat resistance and also there exists a possibility that the quality of products such as printed circuit boards may be impaired by migration of silicone. The fluorine-based films are excellent in heat resistance and mold releasing property but are expensive and have a problem of poor workability owing to low rigidity. Although a crosslinked

resin-type mold releasing film is proposed, its flame resistance and rigidity are not sufficient and it involves a problem that a complex process, i.e., a crosslinking step is required. (See Patent Documents 1 to 4.)

[0004]

[Patent Document 1] JP 2000-263724 A

[Patent Document 2] JP 2003-001772 A

[Patent Document 3] JP 2003-053896 A

[Patent Document 4] JP 2003-012829 A

[0005]

[Problems that the Invention is to Solve]

The present invention provides a mold releasing film suitable for production of flexible printed circuit boards, which is excellent in mold-releasing property, flame resistance, anti-moisture absorbing property, heat resistance, and rigidity.

[0006]

[Means for Solving the Problems]

As a result of extensive studies on technologies to achieve the above object, the present inventors have found that a monolayer film comprising a resin composition containing a polyphenylene ether-based resin as a main component is excellent in mold-releasing property, flame resistance, anti-moisture absorbing property, thermal

resistance and rigidity, and thus a mold releasing film which is suitable for production of flexible printed circuit boards is obtained. Thus, the present invention has been completed.

Namely, the present invention provides:

1. A mold releasing film for printed circuit board production, which is a monolayer film comprising a resin composition containing (A) a polyphenylene ether-based resin in an amount of 50 wt% or more;

2. A mold releasing film for printed circuit board production, which is a monolayer film comprising a resin composition containing (A) a polyphenylene ether-based resin in an amount of 50 to 99.5 parts by weight and (B) a liquid crystalline polyester in an amount of 0.5 to 50 parts by weight;

[0007]

3. The mold releasing film for printed circuit board production according to the above-described 2, having a resin composition containing (C) a compound containing monovalent, divalent, trivalent or tetravalent metal element, in an amount of 0.1 to 10 parts by weight per 100 parts by weight of the total weight of components (A) and (B);

4. The mold releasing film for printed circuit board production according to the above-described 3, characterized in that the monovalent, divalent, trivalent or tetravalent metal element (C) is a Zn element and/or Mg element;

5. The mold releasing film for printed circuit board production according to any one of the above-described 2 to 4, having a resin composition containing (D) a silane compound in an amount of 0.1 to 5 parts by weight per 100 parts by weight of the total weight of components (A) and (B);

[0008]

6. The mold releasing film for printed circuit board production according to the above-described 5, characterized in that the silane compound (D) has an amino group;

7. The mold releasing film for printed circuit board production according to any one of the above-described 1 to 6, characterized in that the monolayer film is obtained by molding through an extrusion tubular method; and

8. The mold releasing film for printed circuit board production according to any one of the above-described 1 to 6, characterized in that the monolayer film is obtained by molding through a T-die extrusion method.



[0009]

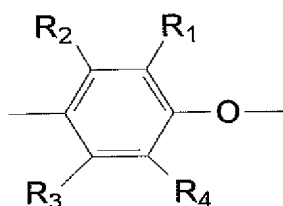
[Mode for Carrying Out the Invention]

The present invention is described in detail below.

The polyphenylene ether-based resin (A) of the invention comprises a repeating unit of formula (1):

[0010]

[Chemical formula 1]



(1)

[0011]

wherein R<sub>1</sub> and R<sub>4</sub> each independently represent hydrogen, primary or secondary lower alkyl, phenyl, aminoalkyl, or hydrocarbonoxy; R<sub>2</sub> and R<sub>3</sub> each independently represent hydrogen, primary or secondary lower alkyl, or phenyl. The resin is a homopolymer and/or copolymer having a reduced viscosity (0.5 g/dl, chloroform solution, measured at 30°C) in the range of 0.15 to 1.0 dl/g. The reduced viscosity is more preferably in the range of 0.20 to 0.70 dl/g, most preferably in the range of 0.40 to 0.60 dl/g.

[0012]

Specific examples of the polyphenylene ether-based resin include, for example, poly(2,6-dimethyl-1,4-phenylene ether), poly(2-methyl-6-ethyl-1,4-phenylene ether), poly(2-

methyl-6-phenyl-1,4-phenylene ether) and poly(2,6-dichloro-1,4-phenylene ether), and further include polyphenylene ether copolymers such as copolymers of 2,6-dimethylphenol with the other phenols, e.g., 2,3,6-trimethylphenol and 2-methyl-6-butylphenol. Of these, preferred are poly(2,6-dimethyl-1,4-phenylene ether) and a copolymer of 2,6-dimethylphenol with 2,3,6-trimethylphenol, and more preferred is poly(2,6-dimethyl-1,4-phenylene ether).

[0013]

As an example of the process for producing the polyphenylene ether (A) for use in the invention, a method of oxidative polymerization of 2,6-xylenol using, as a catalyst, a complex of cuprous salt with an amine as described in U.S. Patent No. 3306874 can be cited. The methods described in U.S. Patent Nos. 3306875, 3257357 and 3257358, JP 52-017880 B, JP 50-051197 A and JP 63-152628 A are also preferred as the methods for producing the polyphenylene ether (A).

The polyphenylene ether-based resin (A) of the invention may be used in the form of a powder after the polymerization step or in the form of pellets obtained by melt-kneading under a nitrogen atmosphere or a non-nitrogen atmosphere or under degassed or non-degassed conditions using an extruder.

[0014]

The polyphenylene ether-based resin (A) of the invention also includes polyphenylene ethers functionalized with various dienophile compounds. Examples of the dienophile compounds include, for example, maleic anhydride, maleic acid, fumaric acid, phenylmaleimide, itaconic acid, acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, glycidyl acrylate, glycidyl methacrylate, stearyl acrylate, and styrene. Furthermore, as the method for functionalization with these dienophile compounds, the functionalization may be carried out in a molten state under degassed or non-degassed conditions in the presence or absence of a radical generator using an extruder. Alternatively, the functionalization may be carried out in a non-molten state, i.e., within the temperature range of room temperature to the melting point in the presence or absence of a radical generator. At this time, the melting point of a polyphenylene ether is defined as the peak-top temperature of a peak observed in a temperature-thermal flow graph obtained by differential scanning calorimeter (DSC) measurement at a temperature elevation rate of 20°C/minute. When two or more of the peak-top temperatures are observed, the melting point is defined as the highest temperature thereof.

[0015]

The polyphenylene ether-based resin (A) of the invention is a polyphenylene ether resin alone or a mixture of a polyphenylene ether resin and an aromatic vinyl polymer and also includes those further mixed with other resins. Examples of the aromatic vinyl polymer include, for example, atactic polystyrene, high-impact polystyrene, syndiotactic polystyrene, and acrylonitrile-styrene copolymers. In the case of using a mixture of a polyphenylene ether resin and an aromatic vinyl polymer, the content of the polyphenylene ether resin is 70 wt% or more, preferably 80 wt% or more, more preferably 90 wt% or more based on the total amount of the polyphenylene ether resin and an aromatic vinyl polymer.

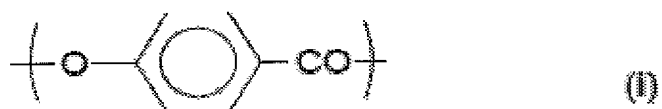
[0016]

The liquid crystalline polyester (B) of the invention is a polyester called a thermotropic liquid crystalline polymer. A known one can be used. Examples thereof include, for example, a thermotropic liquid crystalline polyester containing p-hydroxybenzoic acid and polyethylene terephthalate as main constitutional units, a thermotropic liquid crystalline polyester containing p-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid as main constitutional units, and a thermotropic liquid crystalline polyester

containing p-hydroxybenzoic acid and 4,4'-dihydroxybiphenyl and terephthalic acid as main constitutional units, but the liquid crystalline polyester is not particularly limited. As the liquid crystalline polyester (B) for use in the invention, a polyester comprising the following structural units (i), (ii), and if necessary, (iii) and/or (iv) is preferably used.

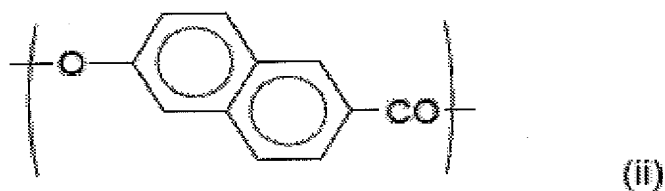
[0017]

[Chemical formula 2]



[0018]

[Chemical formula 3]



[0019]

[Chemical formula 4]



[0020]

[Chemical formula 5]

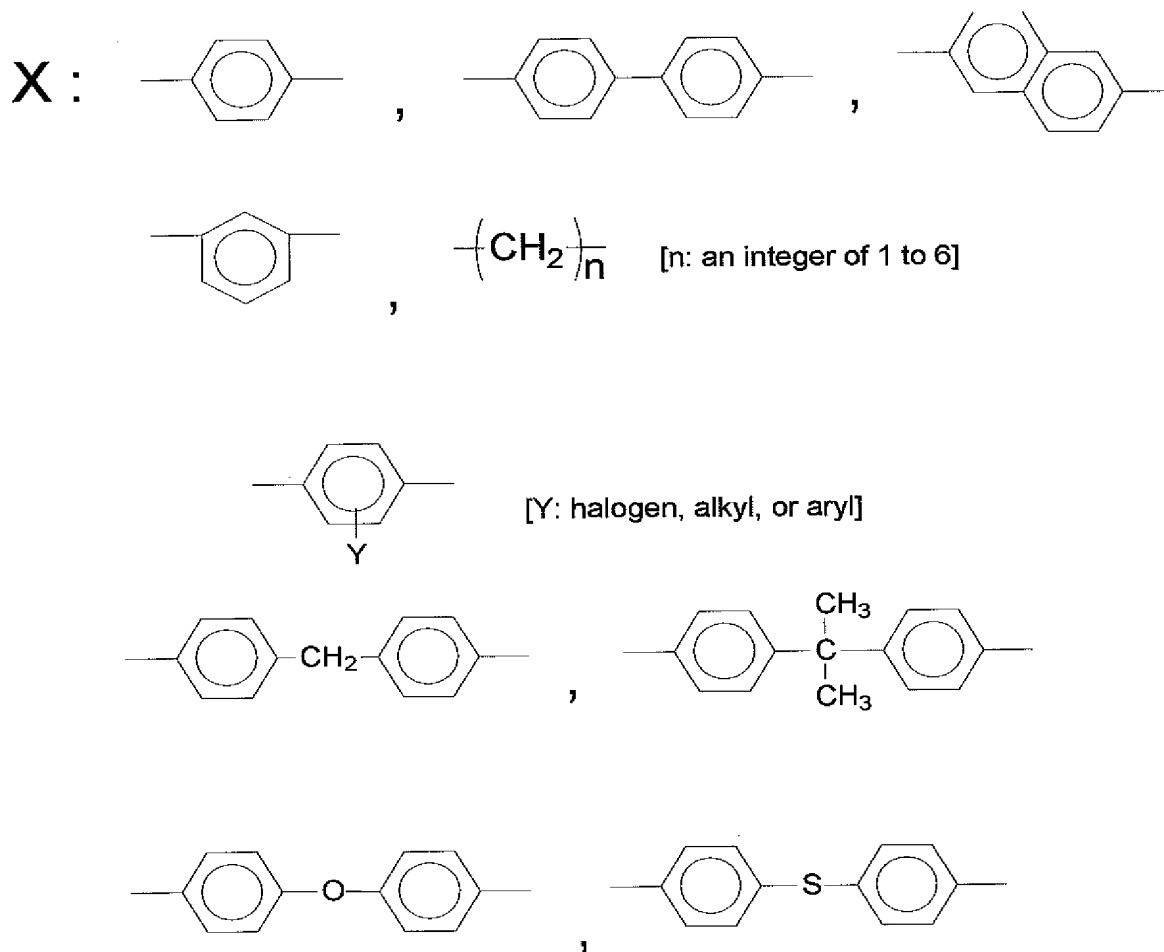


[0021]

The structural units (i) and (ii) are a polyester structural unit formed from p-hydroxybenzoic acid and a structural unit formed from 2-hydroxy-6-naphthoic acid, respectively. Use of the structural units (i) and (ii) can afford a thermoplastic resin composition of the invention excellent in the balance of mechanical properties such as thermal resistance, flowability and rigidity. The X in the above structural units (iii) and (iv) may be any one or two or more selected from the following formula (2).

[0022]

[Chemical formula 6]



... (2)

[0023]

In the structural formula (iii), preferred are structural units formed from ethylene glycol, hydroquinone, 4,4'-dihydroxybiphenyl, 2,6-dihydroxynaphthalene, and bisphenol A, respectively, more preferred are from ethylene glycol, 4,4'-dihydroxybiphenyl, and hydroquinone, and particularly preferred are from ethylene glycol and 4,4'-

dihydroxybiphenyl. In the structural formula (iv), preferred are structural units formed from terephthalic acid, isophthalic acid, and 2,6-dicarboxynaphthalene, respectively, and more preferred are from terephthalic acid and isophthalic acid.

[0024]

As the structural formula (iii) or (iv), the above structural units may be used at least singly or in combination of two or more thereof. In the case that two or more of them are used in combination, specific examples of the structural formula (iii) include, for example, 1) the structural unit formed from ethylene glycol/the structural unit formed from hydroquinone, 2) the structural unit formed from ethylene glycol/the structural unit formed from 4,4'-dihydroxybiphenyl, and 3) the structural unit formed from hydroquinone/the structural unit formed from 4,4'-dihydroxybiphenyl.

[0025]

Moreover, examples of the structural formula (iv) include, for example, 1) the structural unit formed from terephthalic acid/the structural unit formed from isophthalic acid, and 2) the structural unit formed from terephthalic acid/the structural unit formed from 2,6-dicarboxynaphthalene. The amount of terephthalic acid is



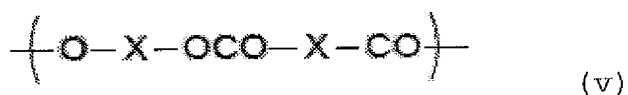
preferably 40 wt% or more, more preferably 60 wt% or more, particularly preferably 80 wt% or more based on the two components. The use of the amount of terephthalic acid of 40 wt% or more based on the two components results in a resin composition exhibiting relatively good flowability and heat resistance. The ratio of the structural units (i), (ii), (iii) and (iv) in the liquid crystalline polyester (B) component is not particularly limited. However, the amounts of the structural units (iii) and (iv) are, in principle, almost equimolar.

[0026]

Furthermore, a structural unit (v) composed of the structural units (iii) and (iv) may be used as a structural unit in component (B). Specific examples thereof include, for example, 1) the structural unit formed from ethylene glycol and terephthalic acid, 2) the structural unit formed from hydroquinone and terephthalic acid, 3) the structural unit formed from 4,4'-dihydroxybiphenyl and terephthalic acid, 4) the structural unit formed from 4,4'-dihydroxybiphenyl and isophthalic acid, and 5) the structural unit formed from bisphenol A and terephthalic acid.

[0027]

[Chemical formula 7]



[0028]

Into the liquid crystalline polyester component (B) of the invention, a structural unit formed from other aromatic dicarboxylic acids, aromatic diols, and/or aromatic hydroxycarboxylic acids, can be introduced as needed in the range of such a small amount that does not impair the characteristics and advantages of the invention.

The temperature at which component (B) of the invention starts to exhibit a liquid crystalline state upon melting (hereinafter referred to as liquid crystal-starting temperature) is preferably from 150 to 350°C, more preferably from 180 to 320°C. To control the liquid crystal-starting temperature within this range is preferable since the amount of black foreign substances is reduced in the resulting resin sheet.

[0029]

The compound (C) containing monovalent, divalent, trivalent or tetravalent metal element of the invention is an inorganic compound or an organic compound containing monovalent, divalent, trivalent or tetravalent metal. Component (C) of the invention is a compound essentially

containing a metal element as a main constitutional component. Specific examples of the metal element capable of being monovalent, divalent, trivalent or tetravalent in component (C) include Li, Na, K, Zn, Cd, Sn, Cu, Ni, Pd, Co, Fe, Ru, Mn, Pb, Mg, Ca, Sr, Ba, Al, Ti, Ge, and Sb. Of these, preferred are elements of Zn, Mg, Ti, Pb, Cd, Sn, Sb, Ni, Al and Ge, and further preferred are elements of Zn, Mg and Ti. From the viewpoints of no peeling of the resin composition or the film itself and a great improvement in the toughness of the film, it is particularly preferred that the monovalent, divalent, trivalent, or tetravalent metal element is Zn element and/or Mg element.

[0030]

As specific examples of the compound (C) containing monovalent, divalent, trivalent or tetravalent metal element, oxides, hydroxides, alkoxide salts, aliphatic carboxylate salts and acetate salts of the above-mentioned metal elements are desirable. Furthermore, examples of preferable oxides include, for example, ZnO, MgO, TiO<sub>4</sub>, TiO<sub>2</sub>, PbO, CdO, SnO, SbO, Sb<sub>2</sub>O<sub>3</sub>, NiO, Al<sub>2</sub>O<sub>3</sub>, and GeO. In addition, examples of preferable hydroxides include, for example, Zn(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, Ti(OH)<sub>4</sub>, Ti(OH)<sub>2</sub>, Pb(OH)<sub>2</sub>, Cd(OH)<sub>2</sub>, Sn(OH)<sub>2</sub>, Sb(OH)<sub>2</sub>, Sb(OH)<sub>3</sub>, Ni(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, and Ge(OH)<sub>2</sub>. Moreover, examples of preferable alkoxide salts include,

for example,  $\text{Ti}(\text{O}^i\text{Pr})_4$  and  $\text{Ti}(\text{O}^n\text{Bu})_4$ . Furthermore, examples of preferable aliphatic carboxylate salts include, for example, zinc stearate, magnesium stearate, titanium stearate, lead stearate, cadmium stearate, tin stearate, antimony stearate, nickel stearate, aluminum stearate, and germanium stearate. Of these, particularly preferable specific examples include  $\text{ZnO}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$ ,  $\text{Ti}(\text{O}^n\text{Bu})_4$ , zinc acetate, zinc stearate, and aluminum stearate. Furthermore, from the viewpoint of no layer peeling,  $\text{ZnO}$  and  $\text{Mg}(\text{OH})_2$  are preferred. Moreover, these components (C) may contain impurities within the range where the advantages of the invention are not impaired.

[0031]

The silane compound (D) of the invention means a silane compound having a functional group, which is a silane compound having at least one functional group selected from the group consisting of an amino group, a ureido group, an epoxy group, an isocyanate group, and a mercapto group. The silane compound having a functional group may be usually a silane compound having any one of these functional groups in the molecule and optionally, it may be a silane compound having two or more of these functional groups in the molecule.

[0032]

Moreover, the silane compound for use in the invention is usually an alkoxysilane having the above functional group in the molecule. Specific examples of the silane compound having a functional group include, for example, silane compounds containing an amino group, such as  $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -aminopropylmethyldimethoxysilane, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane, and  $\gamma$ -phenyl- $\gamma$ -aminopropyltrimethoxysilane; silane compounds having a ureido group, such as  $\gamma$ -ureidopropyltrimethoxysilane,  $\gamma$ -ureidopropylmethyltrimethoxysilane,  $\gamma$ -ureidopropyltriethoxysilane,  $\gamma$ -ureidopropylmethyltriethoxysilane, and  $\gamma$ -(2-ureidoethyl)aminopropyltrimethoxysilane; silane compounds having an epoxy group, such as  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyldimethylmethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and  $\beta$ -(3,4-epoxycyclohexyl)ethyltriethoxysilane; silane compounds having an isocyanate group, such as  $\gamma$ -

isocyanatopropyltrimethoxysilane,  $\gamma$ -  
isocyanatopropylmethyldimethoxysilane,  $\gamma$ -  
isocyanatopropyltriethoxysilane,  $\gamma$ -  
isocyanatopropylmethyldiethoxysilane,  $\gamma$ -  
isocyanatopropylethyldimethoxysilane,  $\gamma$ -  
isocyanatopropylethyldiethoxysilane, and  $\gamma$ -  
isocyanatopropyltrichlorosilane; and silane compounds  
having a mercapto group, such as  $\gamma$ -  
mercaptopropylmethyldimethoxysilane,  $\gamma$ -  
mercaptopropyltriethoxysilane,  $\gamma$ -  
mercaptopropylethyldiethoxysilane,  $\gamma$ -  
mercaptopropylmethyldiethoxysilane,  $\beta$ -  
mercaptoethyltrimethoxysilane,  $\beta$ -  
mercaptoethyltriethoxysilane, and  $\beta$ -  
mercaptoethyldimethoxysilane.

[0033]

Furthermore, from the viewpoint of the toughness of the film, the silane compounds having an amino group are preferred. Namely,  $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -aminopropylmethyldimethoxysilane, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane, and N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane are preferred.

The resin composition of the film in the invention contains a polyphenylene ether-based resin in an amount of 50 wt% or more. From the viewpoints of the heat resistance, flame resistance, mold releasing property and anti-moisture absorbing property of the film, the content is preferably 60% or more, and more preferably 70% or more.

[0034]

The mixing amount of the polyphenylene ether-based resin (A) is from 50 to 99.5 parts by weight, preferably 60 to 99 parts by weight, more preferably 70 to 98 parts by weight. When the mixing amount is more than 99.5 parts by weight, the flowability significantly lowers, and from the viewpoint of the torque (load on an extruder), the set temperature of the extruder is needed to be higher, whereby black foreign substances contained in the film increase. When the mixing amount is less than 50 parts by weight, unevenness of film thickness worsens, and the layer peeling of the film becomes remarkable. The black foreign substances used herein are those referred to as black spot, torrid, and char, and give the film undesirable affect.

[0035]

The mixing amount of the liquid crystalline polyester of component (B) in the invention is from 0.5 to 50 parts by weight, preferably 1 to 40 parts by weight, more

preferably 2 to 30 parts by weight. When the mixing amount is more than 50 parts by weight, unevenness of film thickness worsens due to anisotropy of the liquid crystalline. When the mixing amount is less than 0.5 parts by weight, the flowability significantly lowers, and black foreign substances in the film increase. From the viewpoints of the mold releasing property with a polyimide film as a base film of a flexible printed circuit board and rigidity, the liquid crystalline polyester is preferably mixed in an amount of the above range.

[0036]

The mixing amount of component (C) in the invention is preferably from 0.1 to 10 parts by weight, more preferably 0.2 to 5 parts by weight, particularly preferably 0.4 to 3 parts by weight per 100 parts by weight of total of components (A) and (B). When the content of component (C) is less than 0.1 part by weight, the layer peeling of the film itself becomes remarkable and when the content is more than 10 parts by weight, sometimes, the specific gravity increases and heat resistance decreases.

The mixing amount of component (D) in the invention is preferably from 0.1 to 5 parts by weight, more preferably 0.15 to 3 parts by weight, particularly preferably 0.2 to 1 parts by weight per 100 parts by weight



of total of components (A) and (B). When the content of component (D) is less than 0.1 part by weight, the layer peeling of the film itself becomes remarkable and when the content is more than 5 parts by weight, sometimes, the composition of the invention is not stably obtained.

[0037]

In the invention, in addition to the above components, it is possible to add other additional components within the range where the characteristics and advantages of the invention are not impaired. Examples thereof include, for example, an antioxidant; a flame retardant, e.g., an organic phosphate ester compound, a phosphazene compound, a silicone compound; an elastomer, e.g., an olefin copolymer such as an ethylene/propylene copolymer, an ethylene/1-butene copolymer, an ethylene/propylene/non-conjugated diene copolymer, an ethylene/ethyl acrylate copolymer, an ethylene/glycidyl methacrylate copolymer, an ethylene/vinyl acetate/glycidyl methacrylate copolymer, an ethylene/propylene-g-maleic anhydride copolymer, or ABS, a polyester polyether elastomer, a polyester polyester elastomer, an aromatic vinyl compound-conjugated diene compound block copolymer, or a hydrogenation product of the aromatic vinyl compound-conjugated diene compound block copolymer; a plasticizer such as oil, low molecular weight

polyethylene, epoxidized soybean oil, polyethylene glycol, or an aliphatic ester; a flame retardant aid; a weather (light) resistance improver, various colorants, and a mold releasing agent.

[0038]

The film for printed circuit board production of the invention is a thermoplastic monolayer film containing the above resin composition. The thickness of the film is from 3 to 200  $\mu\text{m}$ . From the viewpoint of cost and handling, it is more preferably from 10 to 100  $\mu\text{m}$ , particularly preferably from 20 to 50  $\mu\text{m}$ .

The resin composition of the invention can be produced by various methods. Examples include, for example, thermal melt-kneading methods by means of a single-screw extruder, twin-screw extruder, a roller, a kneader, a Brabender plastograph, and a Banbury mixer. Of these, a melt-kneading method using a twin-screw extruder is most preferable. The melt-kneading temperature at the time is not particularly limited and may be usually selected from the range of 150 to 350°C.

[0039]

The mold releasing film for printed circuit board production according to the invention can be obtained by extrusion film molding using the resin composition obtained

as described above as a starting material or by charging components constituting the resin composition of the invention directly to an extrusion film molding machine and carrying out the blending and film molding simultaneously.

The mold releasing film for printed circuit board production according to the invention can be produced by an extrusion tubular method, or optionally by a method called inflation molding. For forming a sheet having an even sheet thickness without layer peeling, it is very important to regulate the temperature of a parison, which is suitably selected from the temperature range of 50 to 290°C, so that the parison coming out of a cylinder is not immediately cooled.

[0040]

On the other hand, the mold releasing film for printed circuit board production according to the invention can be produced by T-die extrusion molding. In this case, the film may be used without orientation or may be obtained with uniaxial orientation or biaxial orientation. In the case that increased strength and rigidity of the sheet is desired, orientation is effective.

The thus obtained mold releasing film for printed circuit board production according to the invention is a mold releasing film suitable for production of flexible

printed circuit boards, which is excellent in mold-releasing property, flame resistance, anti-moisture absorbing property, heat resistance, and rigidity.

[0041]

The present invention will be illustrated with reference to the following Examples, but the invention is not limited thereto unless deviating from the substance thereof.

Production Example 1: Production example of polyphenylene ether (PPE-1)

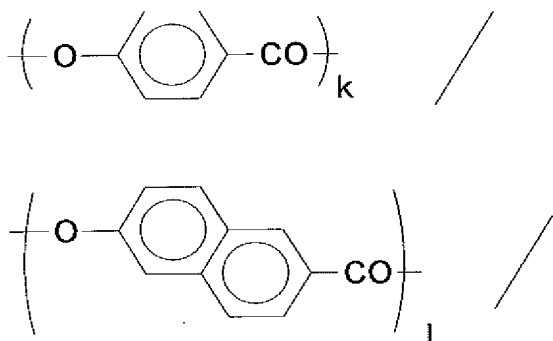
The polyphenylene ether is poly(2,6-dimethyl-1,4-phenylene ether) in a powder form having a reduced viscosity of 0.42, obtained by oxidative polymerization of 2,6-dimethylphenol.

Production Example 2: Production example of liquid crystalline polyester (LCP-1)

A liquid crystalline polyester (LCP-1) having the theoretical structural formula shown below was obtained by charging p-hydroxybenzoic acid, 2-hydroxy-6-naphthoic acid and acetic anhydride under a nitrogen atmosphere and heating and melting the whole to effect polycondensation. The component ratio of the composition is given by molar ratio.

[0042]

[Chemical formula 8]



$$k/l = 0.73/0.27$$

[0043]

The film formation and physical property evaluation of each resin composition were carried out in accordance with the following methods.

(1) Inflation molding

Extrusion sheet molding was carried out with the obtained pellets by a tubular method using an extruder having a screw diameter of 50 mm set at a cylinder temperature of 290°C and a cylindrical die temperature of 290°C. The pressure of blowing air was set so that the thickness became 50  $\mu\text{m}$ .

(2) T-die extrusion molding

Extrusion film molding was carried out with the obtained pellets using a single-screw extruder with a vent having a screw diameter of 65 mm set at a cylinder temperature of 300°C and a T-die temperature of 300°C while

regulating a take-over speed so as to attain a discharging amount of 60 kg/hr, a T-die slit thickness of 0.15 mm, a die slit width of 650 mm, a rolling roller surface temperature of 130°C and a thickness of 50  $\mu\text{m}$ .

[0044]

(3) Mold releasing property

A polyimide film (Kapton (registered trademark) manufactured by Du Pont) having a thickness of 25  $\mu\text{m}$  was used as a base film and a copper foil having a thickness of 35  $\mu\text{m}$  and a width of 50  $\mu\text{m}$  adhered thereto through an epoxy adhesive having a thickness of 20  $\mu\text{m}$  to obtain a copper-clad laminate (i). Next, an epoxy adhesive having a flow-starting temperature of 80°C was applied in a thickness of 20  $\mu\text{m}$  on a polyimide film (Kapton (registered trademark) manufactured by Du Pont) having a thickness of 25  $\mu\text{m}$  to obtain a cover-lay film (ii). A monolayer film having a thickness of 50  $\mu\text{m}$  obtained in the above (1) or (2) was used as a mold releasing film (iii). So that the epoxy adhesive layer of (ii) came into contact with the copper foil side of (i), the films were laminated in the order of (iii), (i), (ii) and (iii) and hot pressing was carried out at 190°C and 50 kgf/cm<sup>2</sup> for 1 minute to obtain a flexible printed circuit board. After the hot pressing, the mold releasing property was judged in accordance with the

following judging criteria at the time when the mold releasing film (iii) was peeled from the polyimide films (i, ii).

A: the film is peeled with no resistance.

B: the film is slightly resistant at the peeling.

C: the film is adhered and not easily peeled off.

[0045]

#### (4) Flame resistance

The form of the films (cylindrical form) and flame were regulated according to the UL-94 film standard of Underwriters Laboratories, and 3 films for each cases were brought into contact with flame once for 3 seconds to judge them in accordance with the following judging criteria.

A: all 3 films were not dropped, and self-extinguished within 10 seconds.

B: the films were dropped once, and self-extinguished.

C: one or more of the films were heavily dropped while keeping burned.

[0046]

#### (5) Anti-moisture absorbing property

The film obtained in the above (1) or (2) was cut into pieces having a size of 100 mm x 190 mm square. After the pieces were exposed under heating and moisturizing conditions of 85°C and 95% relative humidity for 48 hours

using a constant temperature-constant humidity chamber (manufactured by Tabai Espec Corp., PL-3FP), the weight increase rate ( $\Delta w$ ) was determined according to the following equation. An average value of each two films was determined.

Weight increase rate ( $\Delta w$ ) (%) =  $(w_1 - w_0) / w_0 \times 100$   
wherein  $w_1$ : film weight (g) after heating and moisturization,  $w_0$ : film weight (g) after being dried at 100°C for 2 hours in a hot air dryer and cooled to room temperature in a desiccator before heating and moisturization.

A smaller value of the weight increase rate ( $\Delta w$ ) means that the film is excellent in anti-moisture absorbing property.

[0047]

#### (6) Heat resistance

The obtained pellets were molded using an injection molding machine (IS-80EPN: manufactured by Toshiba Machine Co., Ltd.) set at cylinder temperatures of 320/330/320/310°C, an injection rate of 85%, and a mold temperature of 90°C. However, in Comparative Examples 1 and 2, the molding was carried out with all the cylinder temperatures being set at of 280°C. Thus, the pellets were molded into ASTM strip specimens having a size of thickness



3.2 mm x length 127 mm x width 12.7 mm. Using the obtained specimens, the deflection temperature under a load of 0.45 MPa was measured in accordance with ASTM D648.

(7) Rigidity

Using the same specimens as in the above (6), flexural modulus and flexural strength were measured under a temperature atmosphere of 23°C in accordance with ASTM D790 using an autograph (AG-500, manufactured by Shimadzu Corporation).

[0048]

[Example 1]

The polyphenylene ether (PPE-1), the liquid crystalline polyester (LCP-1), and zinc oxide (ZnO, Ginrei-A, manufactured by Toho Zinc Co., Ltd.) were melt-kneaded in a ratio (part(s) by weight) shown in Table 1 to obtain pellets, using a twin-screw extruder (ZSK-25; manufactured by WERNER & PFLEIDERER) with a vent port set at only one barrel temperature at the top-feed side of 250°C and all other barrel temperatures and a die-head temperature of 310°C. Using the pellets, a film having an average thickness of 51  $\mu\text{m}$  was obtained by the inflation molding shown in the above (1). According to the above methods, the film was evaluated. The results are shown in Table 1.

The deflection temperature under load was 184°C and the flexural modulus was 2,670 MPa.

[0049]

[Example 2]

Except that magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ , analytical grade, manufactured by Wako Pure Chemical Industries, Ltd.) was used as the component (C) instead of zinc oxide, pellets were obtained in the same manner as in Example 1. A film having an average thickness of 50  $\mu\text{m}$  was obtained by the T-die extrusion molding shown in the above (2). According to the above methods, the film was evaluated. The results are shown in Table 1. The deflection temperature under load was 183°C and the flexural modulus was 2,650 MPa.

[0050]

[Example 3]

Except that a silane compound having an amino group (silane 1, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane, KBM-602, manufactured by Shin-Etsu Chemical Co., Ltd.) was used as the component (D) instead of zinc oxide and the components were mixed in the ratios (part(s) by weight) shown in Table 1, pellets were obtained in the same manner as in Example 1. A film having an average thickness of 50  $\mu\text{m}$  was obtained by the T-die

extrusion molding shown in the above (2). According to the above methods, the film was evaluated. The results are shown in Table 1. The deflection temperature under load was 182°C and the flexural modulus was 2,590 MPa.

[0051]

[Example 4]

Except that a silane compound having an amino group (silane 2, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane, KBM-603, manufactured by Shin-Etsu Chemical Co., Ltd.) was used as the component (D) instead of zinc oxide and the components were mixed in the ratios (part(s) by weight) shown in Table 1, pellets were obtained in the same manner as in Example 1. A film having an average thickness of 49  $\mu$ m was obtained by the inflation molding shown in the above (1). According to the above methods, the film was evaluated. The results are shown in Table 1. The deflection temperature under load was 180°C and the flexural modulus was 2,550 MPa.

[0052]

[Example 5]

Using a highly heat-resistant modified PPE (manufactured by Asahi Kasei Chemicals Corporation, XYRON X9102 (registered trademark)), an alloy of polyphenylene ether with a polystyrene-based resin, as pellets, a film

having an average thickness of 50  $\mu\text{m}$  was obtained by the inflation molding shown in the above (1). According to the above methods, the film was evaluated. The results are shown in Table 1. The deflection temperature under load was 160°C and the flexural modulus was 2,360 MPa.

[0053]

[Comparative Example 1]

Using a poly(4-methyl-1-pentene) resin (RT18, TPX (registered trademark), manufactured by Mitsui Chemicals Inc.) as pellets, a film having an average thickness of 51  $\mu\text{m}$  was obtained by the inflation molding shown in the above (1). According to the above methods, the film was evaluated. The results are shown in Table 1. The deflection temperature under load was 100°C and the flexural modulus was 1,280 MPa.

[0054]

[Comparative Example 2]

Using a polyethylene terephthalate resin (PET, NEH2050, manufactured by Unitika Ltd.) as pellets, a film having an average thickness of 50  $\mu\text{m}$  was obtained by the T-die extrusion molding shown in the above (2). According to the above methods, the film was evaluated. The results are shown in Table 1. The deflection temperature under load was 75°C and the flexural modulus was 2,420 MPa.

[0055]

[Table 1]

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp. Ex. 1	Comp. Ex. 2
Composition	(A) PPE-1	95	95	95	97			
	(B) LCP-1	5	5	5	3			
	(C) ZnO	0.8						
	(C) Mg(OH) <sub>2</sub>		0.8					
	(D) Silane 1			0.2				
	(D) Silane 2				0.5			
	Modified PPE X9102					100		
Evaluation	TPX						100	
	PET							100
	Mold releasing property	A	A	A	A	A	A	B
	Flame resistance	A	A	A	A	B	C	C
	Anti-moisture absorbing property	0.024	0.026	0.032	0.035	0.043	0.019	0.56
	$\Delta w$ (%)							

[0056]

From the above results, it is found that a monolayer film comprising a resin composition containing a polyphenylene ether-based resin as a main component according to the invention is a mold releasing film suitable for production of flexible printed circuit boards, which is excellent in mold-releasing property, flame resistance, anti-moisture absorbing property, thermal resistance and rigidity.

[0057]

[Advantage of the Invention]

According to the present invention, it becomes possible to provide a mold releasing film suitable for the production of flexible printed circuit boards, which is excellent in mold-releasing property, flame resistance, anti-moisture absorbing property, thermal resistance and rigidity.

[Designation of Document] Abstract

[Abstract]

[Problem] To provide a mold releasing film suitable for the production of flexible printed circuit boards, which is excellent in mold-releasing property, flame resistance, anti-moisture absorbing property, thermal resistance and rigidity.

[Means for Resolution] A mold releasing film for printed circuit board production, which is a monolayer film comprising a resin composition containing (A) a polyphenylene ether-based resin in an amount of 50 wt% or more.

[Selected Drawing] None